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Determination of Graphene Layers by Optical Imaging Contrast Analysis

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ABSTRACT:Practical application of graphene require accurate determination of the number of layers. In this paper we demonstrate a reliable and efficient approach for determining the number of graphene layers. Plots of contrast spectra against number of graphene layers transferred on Borosilicate glass substrates for RGB image, R, G, and B channels were found to increase linearly. The R channel contrast values for one to four graphene layers were found to be 0.076(R), 0.083(R), 0.090(R), and 0.097(R) respectively. Similarly, the G contrast channel values were obtained as -0.032(G), -0.023(G), -0.015(G), and -0.007(G) whereas B channel gives 0.004(B), 0.011(B), 0.019(B), and 0.026(B) for SLG, BLG, Tri-layer and Tetra-layer graphene respectively. The contrast values for SLG in RGB transmission regions were found to be 0.076(R), -0.032 (G), and 0.004(B). Our experimental results deviate from theoretical contrast of SLG transferred on SiO_2 (285 nm)/Si, Quartz, Al_2O_3 (72 nm)/Si and Hexagonal-BN crystal substrate. This deviation is shown to arise from the unappreciable optical absorption of the Borosilicate substrate in the visible spectrum range. Contrast imaging is therefore a reliable method with the R contrast channel providing the highest contrast leading into increased resolution of the detection level of samples.

KEYWORDS:Single-layer graphene, Few-layer graphene, Multilayer graphene, thickness identification, optical contrast.

I. INTRODUCTION

Graphene, which is the basic building block for other graphitic allotropes, has extraordinary optoelectronic properties. The success in isolating multilayer graphene from highly ordered pyrolytic graphite (HOPG) using scotch tape technique has stimulated immense interest in both fundamental physics and graphene-based practical applications. The key to optical identification of the two-dimensional (2D) graphene nanosheets is to correlate its optical [1-3]. The extraordinary optoelectronic properties of graphene arise from its peculiar zero-energy band gap electronic structure in which its electrons exhibit Massless Dirac fermions behaviour in the vicinity of K and K' points of the Brillouin zone [4-6]. There is a significant difference between the properties of single layer graphene (SLG) and bilayer graphene (BLG). For example, the electron mobility of SLG has been approximated to be in the range ~40,000 – 400,000 $cm^2V^{-1}s^{-1}$ whereas the electronic mobility of BLG is approximated to be in the range 3000 – 8000 $cm^2V^{-1}s^{-1}$ [7, 8]. The BLG exhibit band gap tunability leading to high on/off current ratios as compared to SLG. Thus BLG is therefore, preferred to SLG in the fabrication of field effect transistors (FETs) [9]. The optoelectronic properties of few layer graphene (FLG) approach those of graphite as the number of layers exceed 10. This is mainly due to the change in electronic band structures from that of a SLG [9-12]. It has been reported that the optical transparency of FLG is a strong function of the thickness with each SLG having optical absorption of thus rendering the identification and determination of atomic layers in FLG a challenging task [13-15].

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To date, various methods have been developed to determine the number of stacked layers in FLG and MLG samples. These methods include; optical microscopy [13,15], Raman spectroscopy [16,17], Low-energy electron microscopy (LEEM) [18,19], Atomic force microscopy (AFM), transmission electron microscopy (TEM), scanning electron microscopy (SEM) [20], scanning tunnelling microscopy (STM) (21) among others. However, such methods involve time-consuming image analysis processes, expensive equipment, special experimental setups and sample destruction during preparation. In this work, we report contrast spectra analysis as a fast and easy-to-use method for efficient identification and determination of thickness of MLG graphene samples. The optical contrast differences between the MLG samples and the glass substrate serve as a standard reference from which sample thickness is accurately determined without using complex calculations. This method will be key to the study of virtually all 2D layered nanomaterials with thickness-dependence properties in any standard laboratory.

II. EXPERIMENTAL PROCEDURE

The MLG samples were prepared by mechanical exfoliation and transferred to clean Borosilicate substrates. The samples RGB images were observed under an optical microscope (*Labomed LX 400*). Halogen lamp (excitation range 400 – 800 nm) mounted on the microscope was used to generate normal white light through a 1 mm aperture and passed through the MLG samples. A CCD camera fitted on the microscope was used to detect and capture optical RGB images at resolution 1920×1080 pixels. Using ImageJ 1.48v, the contrast between the graphene layers and transmitted light through the samples and capture optical RGB images. The optical contrasts of MLG sheets (C) and substrate C_S were obtained. Grayscale values from RGB images of SLG mounted onto a Fluorine-doped Tin Oxide (FTO) substrate (purchased from Graphene supermarket USA #Y060515) were obtained and used as the standards values. Optical contrast spectrum of the image, R, G, and B channels were calculated based on Fresnel's equations [3, 22].

III. RESULTS AND DISCUSSION

The contrast spectra C were obtained based on Fresnel's equation by the calculation;

$$C = (T_S - T_{MLG})/T_S , \qquad (1)$$

Where T_S and T_{MLG} are the transmission spectrum from the glass substrate and MLG sheets respectively [22, 23]. The contrast spectra for the grayscale optical image (from R, G, and B channels) C_{CsR} , C_{CsG} , and T_{CsB} is calculated by subtracting the contrast of the nanosheets (T_R , T_G and T_B) from that of the substrate (T_{SR} , T_{SG} and T_{SB}) and dividing by contrast of the nanosheets (T_{SR} , T_{SG} and T_{SB}) (Eqn. 2).

$$\begin{aligned} C_{CsR} &= (T_{S\,R} - T_R)/T_{SR} \text{ (R channel)} \\ C_{CsG} &= (T_{SG} - T_G)/T_{SG} \text{ (G channel)} \\ C_{CsB} &= (T_{SB} - T_B)/T_{SB} \text{ (B channel),} \end{aligned} \qquad (2)$$

The absorbance of MLG increases with the number of graphene layers with each graphene layer contributing absorbance of 2.3% [14, 24]. We use the estimated RGB grayscale values for a monolayer (1.98 ± 0.005) which, based on Beer Lambert's law of absorption, correspond to optical transmittance of $98.23\pm1\%$ to determine the number of graphene layers in the MLG samples.In this case,R, G, and B channels were generated from the colour

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images of exfoliated MLG flakes at 100X magnification for clear contrast observation. (Fig. 1(a-d)). Grayscale values obtained along cross-section lines on each image channel show step-like profiles (Fig. 1e).

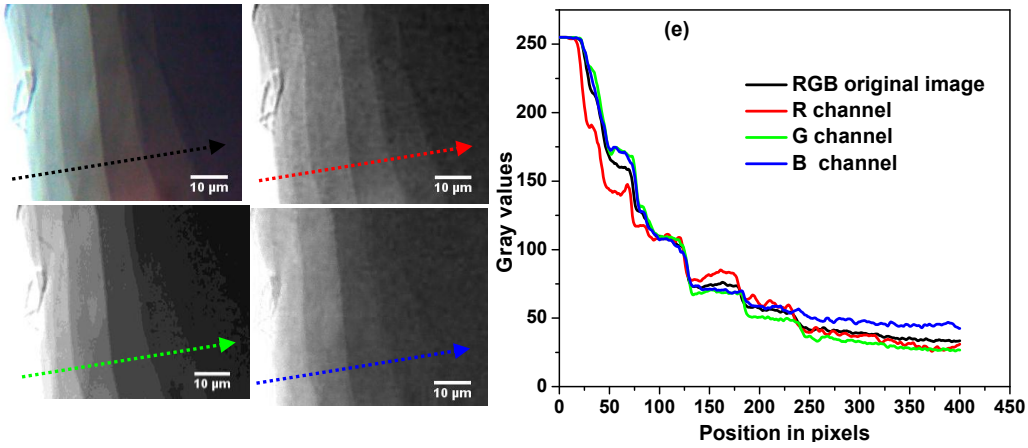

Figure 1. (a) RGB original optical image of graphene sample transferred on Borosilicate glass substrate. (b) – (d) R, G, and B channel images. The R, G, and B channel images were obtained by using the 'image-colour-split channels' functions in the ImageJ software. (e) The grayscale cross section of contrast image corresponding to the dash lines in images (a-d).

Figure 1(a) represents the RGB colour image of 11 to 114 layers of graphene transferred on a glass substrate. The thickness of the optical image is pre-determined through Optical Microscopy. Figures 1(b)–(d) display R, G, and B channel images of the RGB colour image.From the R and B channels image in figure 1(b, d), the contrast values of graphene samples vary with thickness, but the images are blurred. However, for figure 1(c), which shows the G contrast values, a clear contrast is observed.From Fig. 1(e),the profile corresponding to G channel show much higher grayscale values at thin regions and much lower at thick regions. A significant shift in position of the profiles in R, G, and B channels from the RGB image profile is observed. Plots of contrast spectra against number of layers for the RGB image, R, G, and B channels (Fig. 2) exhibit a linear relationship.

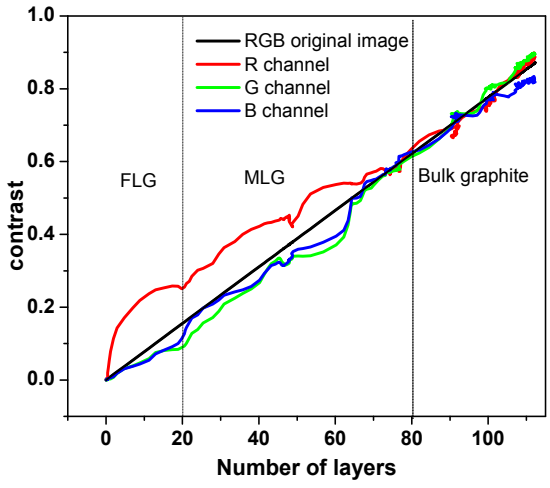

Figure 2: Optical contrast as a function of number of layers for the original RGB optical image, R, G, and B channels.

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From Fig. 2, the curves corresponding to R, G and B channel tend to coincide at a region determined to be approximately 80 layers.The optical contrast is governed by a set of linear equations of the form;

$$C_{CsRGB} = 0.0078\,N - 3.81^{-11} \quad \text{(RGB image)}$$
$$C_{CsR} = 0.0071\,N + 0.0685 \quad \text{(R channel)}$$
$$C_{CsG} = 0.0083\,N - 0.040 \quad \text{(G channel)}$$
$$C_{CsB} = 0.0075\,N - 0.004 \quad \text{(B channel)} \qquad (3)$$

Where C_{CsRGB}, C_{CsR}, C_{CsG}, and C_{CsB} represent contrast spectra for RGB, R, G, and B channels respectively. The R contrast values for SLG, BLG, tri-layer and tetra-layer graphene are 0.076(R), 0.083 (R), 0.090 (R), and 0.097 (R) respectively. The G contrast values for SLG, BLG, tri-layer and tetra-layer graphene are -0.032 (G), -0.023 (G), -0.015 (G), and -0.007 (G) whereas that of B channel are 0.004 (B), 0.011 (B), 0.019(B), and 0.026(B) for SLG, BLG, tri-layer and tetra-layer graphene respectively. From Eqn. 3 the contrast values for a SLG in RGB transmission channels are found to be 0.076 (R), -0.032 (G), and 0.004 (B). Our RGB, R, G, and B experimental results does not march well with the theoretical data as shown in table 1.

Substrate	**R**	**G**	**B**
Borosilicate substrate (Our experimental data)	0.076	-0.32	0.004
SiO_2 (285nm)/Si substrate [22]	0.031	0.077	0.011
Al_2O_3(72 nm)/Si [25]	0.023	0.052	0.119
Quartz [25]	-0.052	-0.060	-0.070
Hexagonal-BN crystal [26]	-0.026	-0.030	-0.035

Table 1: Comparison of R, G, and B channels contrast values with the theoretical contrast values for SLG transferred on different substrates.

From our experiment, the RGB, R, G, and B grayscale values for Borosilicate substrate are constant ≈ 255. This means that the substrate has a negligible optical absorption. From table 1, the intensity of the transmitted light from MLG samples is lower than that from substrate for R and B channels. However, the observed negative G channel contrast values imply that theintensity of the transmitted light from graphene layers is higher than that from the glass substrate. This values were obtained by calculations based on Fresnel's law (Eqn. 1). Therefore, the substrate used has a strong effect on the contrast measurements hence the selection of R, G, and B contrast values should be based on the substrate used. For MLG transferred on Borosilicate glass slides, the average contrast of 0.674(R) in the R range is better than the 0.669(G) and 0.642(B) range and therefore obtaining the contrast in R channel should be considered the best in identifying and counting of the layers. In our method, we propose R channel among the RGB channels since it provides the highest contrast leading into increased resolution of the contrast of MLG samples.

IV. CONCLUSION

We have shown that the contrast spectrum for RGB, R, G, and B channels for MLG samples obtained using mechanical exfoliation can easily be obtained by fitting the number of graphene layers in equation 3. The R channel offers the highest contrast values of graphene samples transferred on Borosilicate glass substrate. From our experiment, we have been able to show the effect of grayscale values of the substrate to the contrast spectra of RGB, R G and B channels. The method reported is fast, easy and unambiguous way to identify the number of graphene layers in MLG samples.

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